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RESERVE PATENT SPECIFICATION

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COMPLETE SPECIFICATION

Dibenzoate Esters of Aliphatic Diols and process for their preparation

CARBIDE CORPORATION, Union (formerly known as Union Carbide and Carbon Corporation), of 30, East 42nd Street, New York, State of New York, United States 5 of America, a corporation organised under the laws of the State of New York, United States of America, (assignee of Gordon Murray Goodale, Edward James Mills, Jr., Thomas Robert Miller and James John 10 FASNACHT), do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a method of pre-paring dibenzoate esters of aliphatic diols by reacting butyl benzoate with an aliphatic diol containing four to nine carbon atoms and having no tertiary hydroxyl groups. A tertiary
20 hydroxyl group is one which is attached to a

tertiary carbon atom.

Among the compounds which may be prepared in accordance with the present invention are the dibenzoate esters of aliphatic diols 25 having an oxygen interrupted carbon chain, such as diethylene glycol dibenzoate, dipropylene giyool dibenzoate, and polyalkylene giyool dibenzoates and the dibenzoate esters of straight and branched chain aliphatic diols straight and branched chain aliphatic diols having an uninterrupted carbon chain, such as 2-ethyl-1,3-heranediol; 2-methoxymethyl-2,4-dimethyl-1,5-pentanediol; 2-ethyl-2-buryl-1,3-propanediol; 2-methyl-2-propyl-1,3-propanediol; 2-diethyl-1,3-propanediol; 2-ethyl-3-methyl-1,5-pentanediol; 2-ethyl-3-methyl-1,5-pentanediol; 2-ethyl-1,5-pentanediol; 2-ethyl-1,5-pentanediol and 1,5-pentanediol and 1,5-pentanediol bibenzoate esters of aliohatic diols of the

Dibenzoate esters of aliphatic diols of the 40 class described above are useful as plasticizers for vinyl resins. Dipropylene glycol dibenzoate is particularly valuable as a plasticizer for polyvinyl chloride resins.

to 9 carbon atoms and which containing no tertiary hydroxyl group can be prepared by reacting one molecular proportion of one of the above described aliphatic diols with 2.5 molecular proportions of butyl benzoate in the presence of an alkaline catalyst. The reaction can be conducted at a temperature of from 100° C, to 250° C, and preferably from 150° C, to 180° C, for a period of from 10 hours to 30 hours. Although the reaction can be conducted at a pressure of from 0.1 mm. Hg to 200 mm. Hg, it is preferably conducted at a pressure of from 2 mm. Hg to 100 mm. Hg. Snimble catalysts for the reaction comprise alkali metal and alkaline earth metal oxides, hydroxides, alkoxides, carbonates and borates. Preferred catalysts are the alkaline earth metal oxides. Calcium oxide is a particularly suitable catalyst because of its good catalytic activity, low cost and ease of handling. Catalyst concentrations can vary from 0.06 per cent by weight to 1.4 per cent by weight but are preweight to 1.4 per cent by weight out are pre-ferably between 0.1 per cent by weight and 1.0 per cent by weight. By operating at a tem-perature in the range of from 158° C. to 180° C. with a catalyst concentration of 0.1 per cent by weight, excellent results are obtained, par-ticularly in the production of dipropylene glycol dibenzoste. As the resction proceeds, butanol is removed by distillation, followed by a mid-fraction, usually containing butanol and butyl benzoate and a third fraction of butyl benzoate. The pure dibenzoate ester of the aliphatic diol can be isolated from the residue by distillation or by filtration.

The following examples are illustrative:-

EXAMPLE I.

Into a three-neck kettle equipped with thermowell, a mechanical stirrer and a 25 × 250 mm. column packed with glass Raschig rings and surmounted by a standard reflux head with nyl chloride resins.

the usual condenser and vacuum receiver attached, were charged 8015 grams (45.0 mols) esters of aliphatic diols which contain from 4 of refined buryl benzoate and 2414 grams (18.0

B.

mois) of dipropylene glycol. Then 104 grams (1.0 per cent by weight of the kettle charge) of calcium oxide were added and the reaction mixture was heated and stirred at a pressure of 100 mm. Hg. Butanol was removed by distillation at this pressure until the kettle temperature increased to 180-194° C. The kettle temperature was then reduced slightly, the pressure was reduced to 50 mm. Hg, and the 10 remaining butanol was collected as distillate. A mid-fraction, containing butanol and butyl benzoate was then distilled, followed by a pure fraction of butyl benzoate. Occasional reductions in pressure were required to facilitate maintenance of the kettle temperature below 198° C. The contents of the reaction kettle were cooled, mixed with a filter aid and filtered to remove the catalyst. The filtrate was then charged to a stripping still equipped with a goose-neck head and an external nitrogen ebullator. The stripping operation was conducted at a temperature of 182° C at less than 1.0 mm. Hg. The kettle residue was then treated with a decolorizing material, filtered, 25 and recovered. A yield of 81.7 per cent of dipropylene glycol dibenzoate (based on dipropylene glycol) was obtained, with an efficiency (based on buryl benzoare) of 86.4 per cent. The refined dipropylene glycol dibenzoare had a purity by saponification of 99.8 per cent, an acidity (as benzoic acid) of 0.02 per cent, a diol content of 0.69 per cent and the following physical properties: Refractive index at 20° C. -Specific gravity (20/20° C.) 1.1255

Example II.

Color (based on Pt-Co scale) 35

Into a three-neck kettle equipped with a 40 thermowell, a mechanical stirrer and a 25×250 mm. column packed with glass Raschig rings and surmounted by a standard reflux head with the usual condenser and vacuum receiver attached, were charged 8015 grams (45.0 mols) 45 of refined buryl benzoate and 2414 grams (18.0 mols) of dipropylene glycol. Then 104 grams (1.0 per cent by weight of the kettle charge) of calcium oxide were added and the reaction mixture was heated and stirred at a pressure 50 of 100 mm. Hg. Butanol was removed by distillation at this pressure until the kettle temperature increased to 175—187° C. The kettle temperature was then reduced slightly, the pressure was reduced to 80 mm. Hg, and the remaining butanol was collected as distillate. A mid-fraction, containing butanol and butyl benzoare was then distilled, followed by a pure fraction of butyl benzoste. Occasional reductions in pressure were required to facilitate maintenance of the kettle temperature below 187° C. The contents of the reaction kettle were cooled, mixed with a filter aid, and filtered to remove the catalyst. The filtrate was then charged to a stripping still equipped with a gooseneck head and an external nitrogen ebullator. The stripping operation was carried out at a temperature of 210° C. and a pressure of 1.5 mm. Hg. The kettle residue was then treated with magnesol, filtered and recovered.

A yield of \$2.6 per cent of dipropylene glycol dibenzoate (based on dipropylene glycol) was obtained, with an efficiency (based on buryl benzoate) of \$7.3 per cent. The refined dipropylene glycol dibenzoate had a purity by saponification of 99.9 per cent, an acidity (as benzoic acid) of 0.06 per cent, a diol content of 0.72 per cent and a color (based on Pt-Co scale) of 35.

EXAMPLE III.

Into a three-neck kettle equipped with a 1

expressed a mechanical stiers and a 25 × 250

thermowell, a mechanical stirrer and a 25×250 mm. column packed with glass Raschig rings and surmounted by a standard reflux head with the usual condenser and vacuum receiver attached, were charged 3565 grams (20.0 mols) of refined butyl benzoate and 1073 grams (8.0 mols) of dipropylene glycol. Then 23 grams (0.5 per cent by weight of the kettle charge) of calcium oxide were added and the reaction mixture was heated and stirred at a pressure of 100 mm. Hg. Butanol was removed by distillation at this pressure until the kettle temperature increased to 175—180° C. The kettle temperature was then reduced slightly, the pressure was reduced to 50 mm. Hg, and the remaining butanol was collected as distillate. A mid-fraction, containing butanol and buryl benzoate was then distilled, followed by a pure fraction of butyl benzoate. Occasional reductions in pressure were required to facilitate 100 maintenance of the kettle temperature below 180° C. After most of the excess butyl benzoare had been collected, the pressure was reduced to 0.5 mm. Hg and the temperature of the kettle was raised as rapidly as possible to 105 around 205—207° C. The desired dipropylene glycol dibenzoate was then collected as distillate

A yield of 86.1 per cent of dipropylene glycol dibenzoate (based on dipropylene glycol) was obtained, with an efficiency (based on butyl benzoate) of 78.8 per cent. The refined dipropylene glycol dibenzoate had a purity (by saponification) of 79.9 per cent, an acidity (as benzoic acid) of 0.05 per cent, a diol content of 0.22 per cent and the following physical properties:—

Refractive index at 20° C. - - 1.5297 Specific gravity (20/20° C.) - - 1.1236 Color (based on Gardner scale) 2.5

Boiling range - - - - 190—195° C. at 0.5 mm. Hg.

120

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EXAMPLE IV.

Into a three-neck kettle equipped with a thermowell, a mechanical stirrer and a 25 × 250 mm. column packed with glass Raschig rings and surmounted by a standard reflux head with the usual condenser and vacuum receiver attached, were charged 3565 grams (20.0 mols) of refined butyl benzoate and 1073 grams (8.0 mols) of dipropylene glycol. Then 4 grams (0.1 per cent by weight of the kettle charge) of calcium oxide were added and the reaction mixture was heated and stirred at a pressure of 100 mm. Hg. Butanol was removed by distillation at this pressure until the kettle temperature was then reduced slightly, the pressure was reduced to 50 mm. Hg, and the remaining butanol was collected as distillate. A mid-fraction, comaining butanol and butyl

Refractive index at 20° C. Specific gravity (20/20° C.) Color (based on Pt-Co scale) Boiling range - -

EXAMPLE V.

40

85

Into a three-neck kettle equipped with a thermowell, a mechanical stirrer and a 25 × 250 mm. column packed with glass Raschig rings and surmounted by a standard reflux head with the usual condenser and vacuum receiver attached, were charged 1782 grams (4.0 mols) 50 of refined buryl benzoate and 537 grams (10.0 mols) of dipropylene glycol. Then 1.26 grams (0.06 per cent by weight of the kettle charge) of calcium oxide were added and the reaction mixture was heated and stirred at a pressure of 55 100 mm. Hg. Butanol was removed by distillation at this pressure until the kentle temperature increased to 175—180° C. The kettle temperature was then reduced slightly, the pressure was reduced to 50 mm. Hg., and the remaining butanol was collected as distil-A mid-fraction, containing butanol and butyl benzoare was then distilled; followed by a pure fraction of butyl benzoate. Occasional

> Refractive index at 20° C. -Specific gravity (20/20° C.) -Color (based on Pr-Co scale) -Boiling range -

EXAMPLE VI

Into a three-neck kettle equipped with a thermowell, a mechanical stirrer and a 25 × 250 mm. column packed with glass Raschig rings and surmounted by a standard reflux head with the usual condenser and vacuum receiver attached, were charged 2228 grams (12.5 mols) of refined buryl benzoate and 531 grams (5.0 mols) of diethylene glycol. Then 2.76 grams (0.1 per cent by weight of the kettle charge) of cakium oxide were added and the reaction mixture was heated and stirred at a pressure of 100 mm. Hg. Butanol was removed by distillation at this pressure until the kettle temperature increased to 175° C.

benzoate was then distilled, followed by a pure fraction of butyl benzoate. Occasional reductions in pressure were required to facilitate maintenance of the kettle temperature around 180° C. After most of the excess butyl benzoate had been collected, the pressure was reduced to 2.0 mm. Hg, and the temperature of the kettle was raised as rapidly as possible to around 215—220° C. The desired ester was then collected as distillare.

A yield of 81.2 per cent of dipropylene glycol dibenzoate (based on dipropylene glycol) was obtained, with an efficiency (based on buryl benzoate) of 90.2 per cent. The refined dipropylene glycol dibenzoate had a purity (by saponification) of 99.9 per cent, an acidity (as benzoate acid) of 0.17 per cent, a diol content of 0.19 per cent and the following physical properties:—

- 1.5287 - 1.1224

210-216° C. at 2 mm. Hg.

reductions in pressure were required to facilitate maintenance of the kettle temperature 65 below 180° C. The contents of the reaction kettle were cooled to 130° C, mixed with a filter aid, and filtered to remove the catalyst. The filtrate was then charged to a stripping still equipped with a guoseneck head and an 70 external nitrogen ebullator. The distillation of dipropylene glycol dibenzoate was carried out at a kettle temperature of 212° C and a pressure above 10 mm. Ho

A yield of 58.1 per cent of dipropylene glycol dibenzoate (based on dipropylene glycol) was obsined, with an efficiency (based on butyl benzoate) of 74.0 per cent. The refined dipropylene glycol dibenzoate had a purity (by sapenification) of 98.5 per cent, an acidity (as benzoic acid) of 0.03 per cent, a diol content of 1.50 per cent and the following physical properties:—

- 1.5282 - 1.1230 - 35

200-204° C. at 1 mm. Hg.

The kettle temperature was then reduced slightly, the pressure was reduced to 50 mm. Hg., and the remaining butanol was collected as distillate. A mid-fraction, containing butanol and butyl benzoate was then distilled, followed by a pure fraction of buryl benzoate. Occasional reductions in pressure were required to facilitate maintenance of the kettle temperature below 180° C. The contents of the reaction kettle were couled to 130° C, mixed with a filter aid and filtered to remove the catalyst. The filtrate was then charged to a stripping still equipped with a gooseneck 115 head and an external nitrogen ebullator. The distillation of diethylene glycol dibenzoate was

15

carried out at a temperature of 210-220° C. and a pressure above 1.0 mm. Hg.

A yield of 73.7 per cent of diethylene glycol dibenzoare (based on diethylene glycol) was obtained, with an efficiency (based on butyl benzoare) of 76.2 per cent. The refined

Refractive index at 20° C. -Specific gravity (20/20° C.) -Color (based on Pt-Co scale) -Boiling range - -

EXAMPLE VII

Into a three-neck kettle equipped with a thermowell, a mechanical stirrer and a 25 × 250 mm. column packed with glass Raschig rings 20 and surmounted by a standard reflex head with the usual condenser and vacuum receiver attached, were charged 2230 grams (12.5 mols) of refined butyl benzoate and 731 grams (5.0 mois) of 2-ethyl-1,3-hexanediol. Then 33 grams (1.0 per cent by weight of the kettle charge) of calcium oxide were added and the reaction mixture was heated and stirred at a pressure of 100 mm. Hg. Butanol was removed by distillation at this pressure until the kerrie temperature increased to 198° C The kettle temperature was then reduced slightly, the pressure was reduced to 50 mm. Hg and the remaining buranol was collected as distillate. A mid-fraction, containing botanol and butyl benzoate was then distilled, followed by a pure fraction of butyl benzoate. Occasional reductions in pressure were required to facilitate maintenance of the kettle temperature around 200° C. After most of the excess butyl benzoate had been collected a stripping operation was carried our for ten minutes at a temperature of 220° C. and a pressure of 1.5 mm. Hg. The kettle residue was then filtered and recovered.

A yield of 88.4 per cent of 2-ethyl-1,3-hexanediol dibenzuare (based on 2-ethyl-1,3-hexanediol) was obtained, with an efficiency (based on buryl benzoare) of 84.0 per cent. The refined 2-ethyl-1,3-hexanediol dibenzuate had a purity (by saponification) of 99.4 per cent, an acidity (as benzoic acid) of 0.14 per cent, a diel content of 0.2 per cent and the following physical properties:—

Specific gravity (20/20° C) — 1.0801

55 Color (based on Gardner scale) — 5

EXAMPLE VIII

Into a three-neck kettle equipped with a thermowell, a mechanical stirrer and a 25×250 mm. column packed with glass Raschig rings and surmounted by a standard reflux head with the usual condenser and vacuum receiver attached, were charged 2230 grams (12.5 mels) of refined buryl henzoate and 731 grams (5.0 mols) of 2-ethyl-1,3-hesanediol. Then 30 grams (1.0 per cent by weight of the kettle charge) of calcium oxide were added and the reaction mixture was heated and stirred at a

diethylene glycol dibenzoate had a purity (by saponification) of 98.9 per cent, an acidity (as benzoic acid) of 0.07 per cent, a diol content of 1.0 per cent and the following physical properties:—

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1.5438 1.1746 80

200-214° C. at 1 mm. Hg.

pressure of 100 mm. Hg. Butanol was removed by distillation at this pressure until the kettle temperature increased to 196° C. The kettle The kettle temperature was then reduced slightly, the pressure was reduced to 50 mm. Hg., and the remaining butanol was collected as distillate. A mid-fraction, containing butanol and butyl benzoare was then distilled, followed by a pure 75 fraction of butyl benzoate. Occasional reductions in pressure were required to facilitate maintenance of the kettle temperature below The contents of the reaction kettle were cooled to around 130° C, mixed with a filter aid and filtered to remove the catalyst. The filtrate was then charged to a stripping still equipped with a gooseneck head and an external nitrogen ebullator. The stripping operation was carried out at 192° C. and 1 mm. Hg. The kettle residue was then filtered and recovered.

A yield of 75.0 per cent of 2-ethyl-1,3-hexanediol dibenzoare (based on 2-ethyl-1,3-hexanediol) was obtained, with an efficiency (based on butyl benzoate) of 77.5 per cent. The refined 2-ethyl-1,3-hexanediol dibenzoate had a purity (by saponification) of 99.0 per cent, an actidity (as benzoic acid) of 0.18 per cent, a diol content of 0.52 per cent and the following physical properties:—

Refractive index at 20° C. — 1.5317

Refractive index at 20° C. - 1.5317
Specific gravity (20/20° C) - 1.0814
Color (based on Gardner scale) - 4

EXAMPLE IX 100 Into a three-neck kettle equipped with a thermowell, a mechanical stirrer and a 25 × 250 mm. column packed with glass Raschig rings and surmounted by a standard reflux head with the usual condenser and vacuum receiver 105 attached, were charged 1068 grams (5.99 mols) of refined buryl benzoate and 441 grams (2.5 mols) of 2-methoxymethyl-2,4-dimethyl-1,5pentanediol. Then 15 grams (1.0 per cent by weight of the kettle charge) of calcium oxide 110 were added and the reaction mixture was heated and stirred at a pressure of 100 mm. Hg. Butanol was removed by distillation at this pressure until the kettle temperature increased to 175—180° C. The kenfe temperature was 115 then reduced slightly, the pressure was reduced to 50 mm. Hg., and the remaining butanol was collected as distillate. A mid-fraction, containing butanol and butyl benzoate was then

105

distilled, followed by a pure fraction of butyl Occasional reductions in pressure were required to facilitate maintenance of the kerrle temperature below 180° C. The conrents of the reaction kettle were cooled to 130° C, mixed with a filter aid and filtered to remove the catalyst. The filtrate was then charged to a stripping still equipped with a gooseneck head and an external nitrogen ebul-Distillation of 2-methoxymethyl-2,4dimethyl-1,5-pentanediol dibenzoate was carried out at a temperature of 232° C. and a pressure of 1.5 mm. Hg.

A yield of 83.1 per cent of 2-methoxymethyl-2,4-dimethyl-1,5-pentanediol dibenzoate (based on 2-methorymethyl-2,4-dimethyl-1,5-pentanediol) was obtained, with an efficiency (based on butyl benzoate) of 79.0 per cent. The refined 2 - methoxymethyl-2,4-dimethyl-1,5pentanediol dibenzoate had a purity (by saponification) of 99.8 per cent an acidity (as benzoic acid) of 0.14 per cent, essentially no diol content and the following physical properties:-

Refractive index at 20° C. Specific gravity (20/20° C) - Color (based on Pt-Co scale) -Boiling point -

25

70

1.5310 1.1003

225° C. at 1.5 mm. Hg.

EXAMPLE X

30 Into a three-neck kettle equipped with a thermowell, a mechanical stirrer and a 25 × 250 mm. column packed with glass Raschig rings and surmounted by a standard reflex head with the usual condenser and vacuum receiver 35 attached, were charged 446 grams (2.5 mols) of refined butyl benzoate and 160 grams (1.0 mols) of 2,4-diethyl-1,5-pentanediol. Then 5 grams of calcium oxide were added and the reaction mixture was heated and stimed at a pressure of 100 mm. Hg. Rutanol was cemoved by distillation at this pressure until the kettle temperature increased to 175-189° The kettle temperature was then reduced slightly, the pressure was reduced to 50 mm. Hg., and the remaining butanol was collected as distillate. A mid-fraction, containing butanol and butyl benzoate was then distilled, followed by a pure fraction of butyl benzoate,

Occasional reductions in pressure required to facilitate maintenance of the kettle temperature below 180° C. The contents of the reaction kettle were cooled to 130° C., mixed with a filter aid and filtered to remove the catalyst. The filtrate was then charged to a stripping still equipped with a gooseneck head and an external nitrogen ebullator. Distillation of 2,4-dicthyl-1,5-pentanediol diben-zoate was carried out at a temperature of 254° C. and a pressure of 4.0 mm. Hg.
A yield of 36.9 per cent of 2,4-diethyl-1,5-

entenedial dibenzoate (based on 2.4-diethyl-1,5-pentanediol) was obtained, with an efficiency (based on butyl benzoate) of 44.8 per cent. The refined 2,4-diethyl-1,5-pentanediol dibenzone had a purity (by saponification) of 99.6 per cent, an acidity (as benzoic acid) of 0.62 per cent, a diol content of 0.04 per cent and the following physical properties:-

Refractive index at 20° C. Specific gravity (20/20° C.) Color (based on Pt-Co scale) Boiling point

1.5322 1.0775 30

206° C, at 1 mm, Hg.

EXAMPLE XI

Into a three-neck kettle equipped with a 75 thermowell, a mechanical stirrer and a 25 × 250 mm. column packed with glass Raschig rings and surmounted by a standard reflux head with and surmounted by a standard remux feeth with the usual condenser and vacuum receiver attached, were charged 8015 grams (45 mols) of refined butyl benzoate and 2125 grams (18 mols) of 3-methyl-1,5-pentanediol. Then 101 grams (1.0 per cent by weight of the kettle charge) of calcium oxide were added and the reaction mixture was heated and stirred at a pressure of 100 mm. Hg. Butanol was removed by distillation at this pressure until the kettle temperature increased to 190-200° The kettle temperature was then reduced slightly, the pressure was reduced to 50 mm. 90 Hg., and the remaining butanol was collected as distillate. A mid-fraction, containing butanol and buryl benroate was then distilled, followed by a pure exaction of butyl benzoate.

Occasional reductions in pressure required to facilitate maintenance of the bettle temperature below 190° C. The contents of the reaction kettle were cooled, mixed with a filter aid and filtered to remove the catalyst. The filtrate was then charged to a stripping still equipped with a gooseneck head and an exter- 100 nal nitrogen ebullator. The stripping operation was carried out at a kettle temperature of 180—189° C. and a pressure of 2 to 4 mm. Hg. The kettle residue was then filtered and

A yield of 85.3 per cent of 3-methyl-1.5pentanediol dibenzoate (based on 3-methyl-1,5pentanediol) was obtained, with an efficiency (based on butyl benzoate) of 86.6 per cent. The refined 3-methyl-1,5-pentanediol dibenzoare had a purity (by saponification) of 100.2 per cent, an acidity (as benzoic acid) of 0.01 per cent, essentially no diol content and the following physical properties:-

Refractive index at 20° C. 1.5378 1.1103 Specific gravity (20/20° C.) Color (based on Pt-Co scale) -70 Boiling range 186--192° C. at 1 mm. Hg. 5 Freezing point -33,4° C. EXAMPLE XII tions in pressure were required to facilitate Into a three-neck kettle equipped with maintenance of the kettle temperature below thermowell, a mechanical stirrer and a 25 x 250 160° C. The contents of the reaction kettle mm. column packed with stainless steel prowere cooled, mixed with a filter aid and filtruded packing and surmounted by a standard tered to remove the catalyst. The filtrate was then charged to a stripping still equipped with a gooseneck head and an external nitrogen reflux head with the usual condenser and vacuum receiver attached, were charged 1338 grams (7.5 mols) of refined butyl benzoare and ebullator. Distillation of 2-ethyl-2-butyl-480 grams (3.0 mols) of 2-cthyl-2-butyl-1,3-propenediol. Then 18.2 grams (1.0 per cent by weight of the kettle charge) of calcium 1,3-propanediol dibenzoate was carried out at a temperature of 237—267° C, and a pressure propanediol. of 1.5 mm. Hg.
A yield of 64.7 per cent of 2-ethyl-2-butyloxide were added and the reaction mixture was heated and stirred at a pressure of 90 mm. 3-propanediol dibenzoate (based on 2-ethyl-Buranol was removed by distillation at 2-butyl-1,3-propanediol) was obtained, with an this pressure until the kettle temperature increased to 140° C. The kettle temperature efficiency (based on butyl benzoate) of 87.4 per cent. The refined 2-ethyl-2-buryl-1,3was then reduced slightly, the pressure was reduced to 75 mm. Hg., and the remaining butanol was collected as distillate. A midpropanedial dibenzoate had a purity (by saponification) of 100.8 per cent, an acidity (as benzoic acid) of 0.02 per cent, died content of 0.39 per cent and the following physical profraction, containing butanol and butyl benzo-ate was then distilled, followed by a pure fracperties:tion of butyl benzoate. Occasional reduc-Refractive index at 20° C. 1,5327 Specific gravity (20/20° C.) - Color (based on Pt-Co scale) -50 1.0778 20 Boiling range 236° C. at 1.5 mm. Hg. distilled, followed by a pure fraction of buryl benzoate. Occasional reductions in pressure EXAMPLE XIII Into a three-neck kettle equipped with a thermowell, a mechanical stirrer and a 25 × 250 were required to facilitate maintenance of the mm. column packed with stainless steel prokettle temperature below 170° C. The contruded packing and surmounted by a standard tents of the reaction kettle were cooled, mixed reflux head with the usual condenser and with a filter aid and filtered to remove the caravacuum receiver attached, were charged 200 grams (1.5 mols) of 2-methyl-2-propyl-1,3-pro-The filtrate was then charged to a stripping still equipped with a gooseneck head and panediol and 670 grams (3.75 mols) of refined an external nitrogen ebullator. Distillation of butyl benzoate. Then 9 grams of calcium oxide (1.0 per cent by weight of the kettle charge) were added and the reaction mixture the ester was carried out at a kettle temperature of 249-252° C. and a pressure of 2.0 nm. Hg.

A yield of 48.2 per cent of 2-methyl-2-propertyl-1,3-propanediol dibenzoate (based on 2-methyl-2-propyl-1,3-propanediol) was obtained. The refined 2-methyl-2-propyl-1,3-propyl-1, was heated and stirred at a pressure of 100 mm. Hg. Butanol was removed by distillation at this pressure until the kettle tempera-ture rose to 156° C. The kettle temperature propanediol dibenzoate had a purity of 101.8 (by saponification), essentially no acidity and diol content and the following physical properwas reduced slightly, the pressure was reduced to 50 mm. Hg., and the remaining butanol was collected as distillate. A mid-fraction, containing butanol and butyl benzoate was then ties:-1.5367 1.1003 Refractive index at 20° C. Specific gravity (20/20° C.) - Color (based on Pt-Co scale) -95 20 214° C. at 2 mm. Hg. -5.6° C. Boiling range Freezing point vacuum receiver attached, were charged 670 grams (3.75 mols) of refined buryl benzoate and 105 200 grams (1.5 mols) of 2,2-diethyl-1,3-propanediol. Then 9 grams of calcium oxide (1.0 per cent by weight of the kettle charge) EXAMPLE XIV In a three-neck kettle equipped with a thermowell, a mechanical stirrer and a 25 × 250 mm. column packed with stainless steel pro-

were added and the reaction mixture was

truded saddles, and surmounted by a standard reflux head with the usual condenser and Marie and the control of the control

heated and stirred at a pressure of 100 mm. Butanol was removed by distillation at pressure until the kettle temperature increased to 165° C. The kettle temperature was then reduced slightly, the pressure was reduced to 50 mm. Hg., and the remaining butanol was collected as distillate, fraction containing butanol and butyl benzo-ate was then distilled, followed by a pure insetion of buryl benzoate. Occasional reductions in pressure were required to facilitate maintenance of the kettle temperature below 184° C. The contents of the reaction kettle were cooled, mixed with a filter aid and filtered to remove the catalyst. The filtrate was then 30 Refractive index at 20° C. Specific gravity (20/20° C.) - Color (based on Pt-Co scale) -

Boiling range -Freezing point -

EXAMPLE XV

35

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Into a three-neck kettle equipped with a thermowell, a mechanical stirrer and a 25 x 250 mm column packed with glass Raschig rings and surmounted by a standard reflux head with the usual condenser and vacuum receiver attached, were charged 802 grams (4.5 mols) of refined butyl benzoate and 236 grams (2.0 mols) of 2-methyl-1,5-pentanedial. grams of calcium oxide (1.0 per cent by weight of the kettle charge) were added and the reaction mixture was heated and stirred at a pres sure of 100 mm. Hg. Butanol was removed by distillation at this pressure until the kettle temperature increased to 171° C. The kettle temperature was reduced slightly, the pressure was reduced to 50 mm. Hg., and the remaining butanol was collected as distillate, mid-fraction, containing butanol and butyl benzoate was then distilled, followed by a pure

Refractive index at 20° C. Specific gravity (20/20° C.) Color (based on Pt-Co scale) -Boiling range Freezing point

EXAMPLE XVI Into a three-neck kettle equipped with a thermowell, a mechanical stirrer and a 25 × 250 mm. column packed with strinless steel protruded packing and surmounted by a standard 85 reflux head with the usual condenser and vacuum receiver attached, were charged 850 grams (4.77 mols) of refined butyl benzoate and 264 grams (2.0 mols) of 2-ethyl-1,5-pen-Then 11 grams of calcium oxide (1.0 per cent by weight of the kettle charge) were added and the reaction mixture was heated and stirred at a pressure of 100 mm. Butanol was removed by distillation at this pressure until the kettle temperature increased to 154° C. The kettle temperature was then reduced slightly, the pressure was reduced to 50 mm. Hg., and the remaining charged to a stripping still equipped with a gooseneck head and an external nitrogen ebullator. Distillation of the ester was carried out at a kettle temperature of 200° C, and a pressure of 2.0 mm. Hg.

A yield of 42.9 per cent of 2,2-diethyl-1,3ropanediol dibenzoste (based on 2,2-diethyl-1,3-propandiol) was obtained, with an efficiency (based on butyl benzoate) of 51.1 per cent. The refined 2,2-diethyl-1,3-propanediol dibenzoate had a purity of 101.2 per cent (by saponification), essentially no acidity, a diol content of 0.34 per cent, and the following physical properties:-

L5402 1.1097 18 -214° C. at 2 mm. Hg. 211 −5° Č.

fraction of butyl benzoate. Occasional reduc- 55 tions in pressure were required to facilitate maintenance of the kettle temperature below The contents of the reactor kettle were cooled, mixed with a filter aid and filtered to remove the catalyst. The filtrate was then charged to a stripping still equipped with a gooseneck head and an external mitrogen chul-Distillation of the ester was carried out at a kettle temperature of 200 to 210° C.

at 2.0 mm. Hg.
A yield of 88.3 per cent of 2-methyl-1,5pentanediol dibenzoate (based on 2-methyl-1,5entanedial) was obtained, with an efficiency of pentanediol) was obtained, whit an emission was 88.8 (based on butyl benzoate). The refined 2-methyl-1,5-pentanediol dibenzoate had a purity of 99.8 per cent (by saponification) an acidity (as benzoic acid) of 0.12, essentially no diol content and the following physical properties: -

1.5379 1.1045 18 -204° C. at 2 mm. Hg. 203--3.8° C.

butanol was collected as distillate. fraction, containing butanol and butyl benzoate was then distilled, followed by a pure fraction of butyl benzoate. Occasional reductions in pressure were required to facilitate maintenance of the lettle temperature below 187° C. The contents of the reaction kettle were cooled, mixed with a filter aid and filtered 105 to remove the catalyst. The filtrate was then charged to a stripping still equipped with a gooseneck head and an external nitrogen ebullator. Distillation of the ester was carried our at a kettle temperature of 218-221° C. 110 and a pressure of 1.5 mm. Hg.

A yield of 89.8 per cent of 2-ethyl-1,5-pen-tanediol dibenzoste (based on 2-ethyl-1,5-pentanediol) was obtained with an efficiency (based on butyl benzoate) of 91.4 per cent.

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	refined 2-ethyl-1,5-pentanediol dibenzoate had a punity (by saponification) of 99.9 per cent, an acidity (as benzoic acid) of 0.13 per cent,	and a diol content of 0.69 per cent, and the following physical properties:—	5
10	Refractive index at 20° C Specific gravity (20/20° C.) - Color (based on Pt-Co scale) - Boiling range Freezing point	- 1.5356 - 1.0945 - 20 - 215—218° C, at 1.5 mm. Hg. - —35° C.	
	EXAMPLE XVII Into a three-neck kettle equipped with a thermowell, a mechanical stirrer and a 25 × 250 mm. column packed with glass Raschig rings	butyl benzoate. Occasional reductions in pressure was required to facilitate mannenance of the kettle temperature below 212° C. The contents of the reaction kettle were cooled,	35
15	and surmounted by a standard reflux head with the usual condenser and vacuum receiver attached, were charged 620 grams (3.48 mols) of refined butyl benzoate and 200 grams (1.31	mixed with a filter aid and filtered to remove the catalyst. The filtrate was then charged to a stripping still equipped with a gooseneck	J J
20	mols) of 2-ethyl-3-methyl-1,5-pentanediol. Then 8 grams (1.0 per cent by weight of the kettle charge) of lime (technical grade calcium	temperature of 217-222° C. and a pressure of 2.0 mm. Hg.	40
25	oxide) were added and the reaction mixture was heated to 110° C. and stirred at a pressure of 100 mm. Hg. Butanol was removed by distillation at this pressure until the kettle temperature increased to 190° C. The kettle	an efficiency (based on butyl benzaate) of 79.7 per cent. The refined 2-ethyl-3-methyl-1,5-	4 5
30	temperature was then reduced slightly, the pressure was reduced, and the remaining butanol was collected as distillate. A mid-fraction, containing butanol and butyl benzoate was then distilled, followed by a pure fraction of	pennanediol dibenzoate had a purity of 98.7 per cent (by saponification), an acidity (as benzoic acid) of 0.12 per cent, a diol content of 0.41 per cent and the following physical properties:—	50
55	Refractive index at 20° C Specific gravity (20/20° C.) - Color (based on Pt-Co scale) - Boiling range Freezing point	- 1.5362 - 1.0945 - 18 - 210—218° C. at 2 mm, Hg. 17.2° C.	
60	WHAT WE CLAIM IS:— 1. Process for preparing dibenzoate esters of aliphatic diods which comprises reacting butyl benzoate with an aliphatic diol contain-	of from 2 mm. of mercury to 100 mm. of mer- cury. 9. Process as claimed in any of Claims 1 to 8 in which the allphatic diol is dipropylene	85
65	ing 4 to 9 carbon atoms and having no tertiary hydroxyl groups as hereinhefore defined. 2. Process as claimed in Claim 1 in which one molecular proportion of the aliphatic diol	giycol. 10. The dibenzoate ester of 2-ethyl-1,3-hexane diol. 11. The dibenzoate ester of 2-methyl-1,5-	90
	is reacted with 2.5 molecular proportions of butyl benzoate. 3. A process as claimed in Claim 1 or 2 in	pentanediol. 12. The dibenzoate ester of 2-ethyl-1,5-pentanediol.	95
70	which the reaction is effected in the presence	13. The dibenzoate ester of 2-ethyl-3-methyl-1,5-pentanediol. 14. The dibenzoate ester of 2,4-diethyl-1,5-pentanediol.	
75	line earth metal oxide, hydroxide, alkoxide, car- bonate or borate. 5. Process as claimed in Claim 4 in which the alkaline earth metal oxide is calcium oxide.	15. The dibenzoate ester of 2-ethyl-2-butyl-1,3-propanodiol. 16. The dibenzoate ester of 2-methyl-2-propyl-1,3-propanediol.	100
80	6. Process as claimed in Claim 3, 4 or 5 in which the catalyst concentration is between 0.1% and 1.0% by weight. 7. Process as claimed in any of Claims 1 to 6 in which the reaction is effected at a tem-	17. Process for preparing dibenzoare esters of aliphatic diols substantially as herein des- cribed with reference to and as illustrated in the foregoing examples.	LO 5
	perature of from 150° C. to 180° C. 8. Process as claimed in any of Claims 1 to 7 in which the reaction is effected at a pressure	W. P. THOMPSON & CO., 12, Church Street, Liverpool, 1, Chartered Patent Agents.	

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